Changes in Rice with Variable Temperature Parboiling: Thermal and Spectroscopic Assessment

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ABSTRACT

Rapid visco analysis (RVA) and differential scannning calorimetry (DSC) provided overall assessments of the effects of variable temperature soaking at 30, 50, 70, and 90°C and steaming at 4, 8, and 12 min. Calculation of the relative parboiling index (RPI) and percent gelatinization provided good metrics for determining the overall effects of partial parboiling. FT-Raman and solid-state ^{13}C CP-MAS NMR spectroscopies provided insight to conformational changes in protein and starch of paddy rice under various parboiling conditions. RVA showed lower pasting curves and DSC showed lower ΔH with increased temperature and steaming times. A large decrease in viscosity occurred with only the 30-4 treatment as opposed to raw rice. This observation was consistent with FT-Raman results that indicated substantial conversion of the protein from α-helix to other conformations. DSC indicated incomplete gelatinization of starch, even with 90°C soaking and 12 min of steaming. Solid-state ^{13}C CP-MAS NMR spectroscopy confirmed this result. However, it indicated the percent of V_h/amorphous plus the remaining crystalline starch in the 90-12 treatment was equal to the amorphous and partially-ordered starch in commercially parboiled rice. These results suggest that partial parboiling, 90°C soaking, and more than 8 min of steaming (ideally ≈12 min) of paddy rice is sufficient to induce changes that inactivate enzymes and provide enough starch gelatinization to prevent kernel breakage.

Parboiling is a hydrothermal process in which the crystalline form of starch present in paddy rice is changed into an amorphous form as a result of the irreversible swelling and fusion of starch. This is accomplished by soaking in hot water and steaming at low pressure, before drying and milling the rice. There are many specific methods of manufacture of parboiled rice, but essentially the processes remain the same (Ramesh et al 2000). The process of parboiling results in physical, chemical, and organoleptic changes in the rice with economic and nutritional advantages (Gariboldi 1974; Kasasian 1982; Bhattacharya 1985; Pillaiyar 1990; Luh and Mickus 1991).

Araullo and de Padua (1976) listed objectives of parboiling as 1) increase the total and head rice yield of paddy; 2) prevent loss of nutrients during milling; 3) salvage wet or damaged rice; and 4) prepare the rice according to the requirements of consumers in certain parts of the world.

Changes that occur in rice during the parboiling process have been recognized. The orderly polygonal structure characteristic of rice starch embedded in a proteinaceous matrix gelatinizes and expands until it fills the surrounding air spaces, becoming a homogenous compact mass (Luh and Mickus 1991) and the enzymes present in the parboiled grains are either partially or entirely inactivated. Parboiled rice that has been stored for 10 months had low free fatty acid content, presumably as a result of the inactivation of lipase (Shaheen et al 1975). The leaching of solids into cooking water and the extent of the solubilization of the kernel on cooking are considerably reduced (Luh and Mickus 1991).

These changes are generally known to affect milling, storage, subsequent cooking and eating properties. Milling yields are higher and levels of brokens are reduced. Grain structure becomes compact and has a vitreous, translucent and shiny appearance as germination is no longer possible and the endosperm has a compact texture. Parboiled paddy and milled rice are resistant to insect attack and to absorption of water from the atmosphere, making them keep better and longer than raw milled rice.

About 60% of the rice produced in Ghana is grown in the northern sector of the country. Harvesting of the crop in this part of the country occurs between December and January when the relative humidity is very low. As a result, several cracks develop in the paddy grains at harvest, resulting in high levels of brokens of milled raw rice. Consequently, almost all the rice produced in northern Ghana is parboiled to avoid excessive breakage on milling. Rice parboiling is a vast artisanal industry in northern Ghana and techniques used are very rudimentary and variable. Hence, this study was set up to mimic the range of environmental and processing conditions that could be expected to be encountered in that region to assess the results of those processes.

Viscometry has often been used to assess the pasting properties of rice. Use of rapid visco analysis (RVA) has become the standard method for industry and breeding programs to determine rice pasting properties (Bergman et al 2004). The parameters of peak viscosity, breakdown, final viscosity, setback time to peak viscosity, and pasting temperature are typically recorded with RVA.

Differential scanning calorimetry (DSC) is the most common thermal method used to assess the gelatinization of starch (Biliaderis et al 1986; Ojeda et al 2000). The parameters generated include gelatinization enthalpy (ΔH); gelatinization onset temperature (T_o), the point at which rapid swelling starts; the halfway transition temperature, midpoint or peak temperature (T_p); and the conclusion temperature (T_c), when the gelatinization is completed.

Previously, Raman spectroscopy has been proven successful for the study of the prediction of protein and amylose content of rice (Himmelsbach et al 2001; Sohn et al 2004). Also, it has been successfully utilized in determining protein conformation in grain (Piot et al 2002). Recently, the bands for the anomeric vibrations associated with both the amylose and amylopectin components in rice have been detected using a two-dimensional approach to improve the results of employing Raman spectroscopy (Liu et al 2004).

Solid-state ^{13}C NMR has been used over almost three decades to investigate starch structure. The cross-polarization magic-angle spinning (CP-MAS) experiment of Schaefer and Stejskal (1976) has been the experimental technique generally employed. An excellent review of the literature related to starch is included in a report by Paris et al (1999) on the behavior of amorphous, native, and recrystallized starches. Decomposition of C1 resonance in amorphous starches (Paris et al 2001), revealed that four types of α-(1→4) exist in amorphous cereal starches. Domain structure and dynamics in native starch granules were studied further by Tang and Hills (2003).

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MATERIALS AND METHODS

Parboiling

TOX 3108 is a commonly cultivated rice cultivar in Ghana, (known locally as *sikamo*), grown at the Irrigation Development Centre, Ashaiman, Ghana, and harvested in December 2001 was used. It took an average of 120 days to maturity and has medium-to-long grain size. This cultivar was parboiled in the laboratory using modified soaking and steaming regimes.

Soaking. Samples (500 g) of paddy rice were soaked in 1,000 mL of water and heated in a sauce pan to temperatures of 30, 50, 70, and 90°C. Each sample was then transferred into a 5-L beaker and kept in a laboratory oven at 30°C for 16 hr (overnight).

Steaming. For each soaking temperature, samples were steamed for 4, 8, and 12 min.

Drying. The steamed paddy rice was then spread on stainless steel trays and dried in a hot air oven (R. Royce Industrial Ovens, Romsey, Hants, England) at 40°C for 4 hr. Trays were removed at the end of every hour for the rice to be thoroughly stirred and the tray positions rotated.

Milling

A 200-g subsample of each sample was first dehusked in a testing rice husker (THU-34A, Satake, Japan). The brown rice obtained was weighed and whitened in a single-pass friction rice pearler (BS08A, Satake, Japan) with the degree of whiteness set at medium on the equipment. The samples were then ground in laboratory sample mill to pass through a 250-μm sieve and used for spectroscopic analyses.

Samples were labeled according to the soaking temperature and steaming time. For example, a sample that had an initial soaking temperature of 90°C and was steamed for 12 min was given the designation of "90-12". The sample designated "raw" was of the same cultivar (TOX3108) that was not parboiled, but was milled and ground in the same manner as those that had been variably parboiled. The "Tilda" sample that was commercially available (Rainham, Essex, UK) was pressure-parboiled (soaked at a constant temperature of 65°C and steamed at a pressure of 4 kg/cm^2 for 20 min). This was ground and analyzed in the same manner as the laboratory-parboiled samples.

Viscometry

Viscometry was conducted using a Rapid Visco Analyzer (RVA) Model 3D (Newport Scientific, Warriewood, Australia) and Thermocline for Windows v.2.3 software. The general pasting method (162, ICC 2004) for flour samples was used, employing 3.225 g of rice flour in 25 mL of distilled water (corrected to compensate for 14% moisture basis correction of sample). The method profile used an initial 50°C temperature setting and a paddle speed of 960 rpm. After 10 sec, the speed was reduced to 160 rpm and after 1 min, the temperature was ramped to 95°C over 4.42 min then ramped down to 50°C starting at 11 min and ending at 13 min. Data was taken every 2 sec. The data was plotted as time versus centipoise (cP).

Starch Damage

Rice flour was substituted for wheat flour in measuring starch damage resulting from the parboiling process utilizing the Megazyme starch damage assay kit K-SDAM (Wicklow, Ireland). The precise procedures followed were in accordance with those provided in Approved Method 76-31 (AACC International 2000) and Method 164 (ICC 2004). Rice flour samples (100 ± 10 mg) were utilized and run in triplicate. Starch damage was calculated as % Starch damage = $\Delta E \times F \times 90 \times 1/1000 \times 100/W \times 162/180 = \Delta E \times F/W \times 8.1$, where: ΔE = absorbance (reaction) read against the reagent blank; F = 100 (μg of glucose)/absorbance of 100 μg of glucose; 90 = volume correction (0.1 mL taken from 9.0 mL); 1/1000 = conversion from micrograms to milligrams, $100/W$ = factor to express starch damage as a percentage of flour weight; W = weight in milligrams (as-is basis) of flour analyzed; and 162/180 = adjustment from free glucose to anhydrous glucose (as occurs in starch).

Relative Parboiling Index (RPI)

Relative parboiling index (RPI) was calculated using regression analysis with the % starch damage as the dependent variable and the initial soaking temperature and steaming time as predictors. The RPI is an indication of the severity of the parboiling process, based on the combination of initial soaking temperature and steaming time. The RPI is based on the equation $y = a\chi_1 + b\chi_2 + c$, where χ_1 = initial soaking temperature, a = the coordinate of the initial soaking temperature, χ_2 = streaming time, b = the coordinate of the steaming time (min), and c = the regression constant. The derived empirical relationship utilized to provide RPI values was RPI = $(4.700 \times 10^{-3} \times \chi_1) + (6.326 \times 10^{-2} \times \chi_2) + 1.217$.

Differential Scanning Calorimetry (DSC)

Rice flour sample (≈3 mg) was accurately weighed into a stainless steel DSC pan and two times its weight of water was added (w/v). The pan was sealed and left to equilibrate at room temperature for 2 hr. The sample was heated in a Perkin Elmer DSC7 at a rate of 10°C/min from 30 to 110°C. The onset temperature (T_o), peak temperature (T_p), and enthalpy of gelatinization (ΔH) (dry basis) were noted as recorded by the instrument. The ΔH was determined from the area under peak after drawing a two-point baseline line from T_o to the T_c. The determinations were made in triplicate and the mean of each calorimetric measurement was reported.

Raman Spectroscopy

Raman spectroscopy was conducted on a Nicolet 950 Raman bench (Thermo Fisher Scientific, Madison, WI) using a 1,064 nm NIR laser source, a CaF_2 beamsplitter, and a liquid N_2 cooled Ge detector. Samples were placed in low-iron NMR tubes. Raman scatter was collected using the 180° reflective mode at 500 mW of laser power at a frequency of 9,398 cm^{-1} over 256 scans at 4 cm^{-1} resolution from 3,994 to 0 cm^{-1} (Stokes region only). All data was collected utilizing Omnic, v.6.2 software (Thermo Fisher Scientific), and apodized with a Happ-Genzel function and corrected with a white light reference spectrum of KBr. Duplicate spectra were collected on each sample in which the sample tube was rotated 180° between repetitions. Replicate spectra were averaged to produce a single spectral data file for each sample.

Averaged spectral data files were truncated to 3,600–200 cm^{-1} Raman shift and imported into GRAMS/AI (Thermo Fisher Scientific). Baseline removal was conducted by way of a locally developed Array Basic macro that automatically found the lowest points within specified spectral ranges and leveled them to zero intensity. Spectral normalization on this data set was accomplished with another locally developed Array Basic macro that automatically measured the total integrated area of the spectrum and normalized it.

The resulting spectral data was subjected to the peak fitting routine available in GRAMS/AI over a 1,566–1,720 cm^{-1} range that included the amide I region. This region was iterated with Gaussian peak fitting allowing a maximum of 20 peaks to a minimum RMS error relative to the original spectral trace. The relative percent contribution of each band to the total area of all the identified bands for amide I was then calculated.

NMR Spectroscopy

Ground rice samples (passed through a 250-μm sieve) were packed into 6 mm o.d. zirconium oxide rotors and spun, at the magic-angle, at 5 kHz. ^{13}C solid-state NMR spectra were recorded using a 300 MHz, Jeol JNM E CP 300 Fourier Transform NMR spectrometer (JEOL) equipped with a 6-mm SH30T6/HS solid-

state probe. The magnetic field strength was 7.05 T and the resonance frequency for ^{13}C was 75.57 MHz. Spectra were acquired using a CP-MAS pulse sequence, incorporating a 4-μsec pulse width, a relaxation delay of 10 sec, and a contact time of 3 msec. Carbon NMR data was reported to the nearest 1 ppm and referenced to the methyl resonance of DSS (sodium 2, 2-dimethyl-2-silapentane-5-sulfonate) set to 0 ppm.

The resulting spectral data was imported into the GRAMS/AI, smoothed with a 20-point smooth and subjected to Fourier self-deconvolution over a range of 108–90 ppm, anomeric (C1) region for starch, using a $\gamma = 1$ and typically 60% smoothing with a Bessel function. After baseline correction, it was subjected to the peak-fitting routine to find a maximum of 10 peaks (over the same region) and iterated against mixed Gaussian/Lorentzian peak shapes to minimum RMS error relative to the original spectral trace. The relative peak area for each peak was calculated over the investigated region.

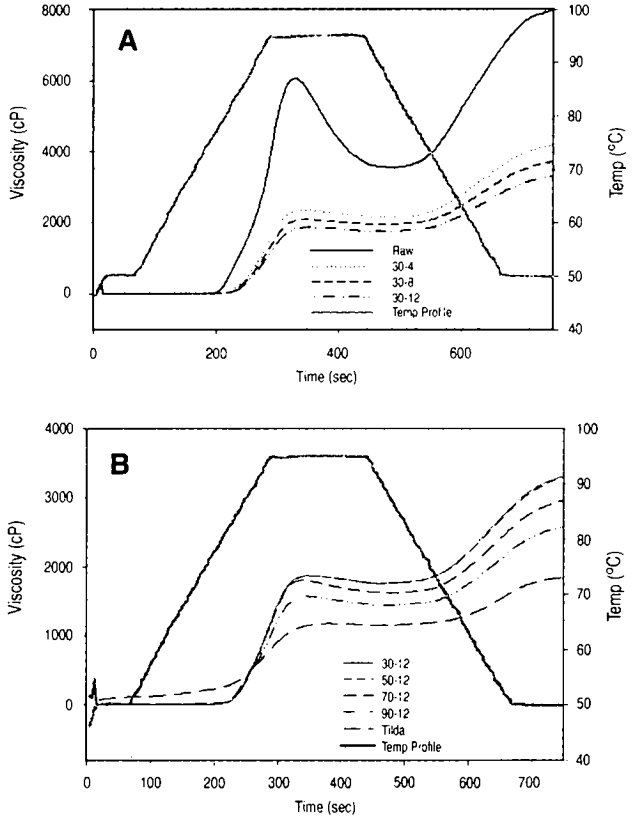

Fig. 1A, RVA patterns of raw rice plus samples soaked at 30°C and steamed for 4, 8, and 12 min. **B,** RVA patterns of rice soaked at 30, 50, 70, and 90°C all steamed for 12 min vs. commercially parboiled rice (Tilda).

RESULTS AND DISCUSSION

Parboiling has a marked effect on the pasting behavior of rice (Ali and Bhattacharya 1980). Pasting temperature is raised, while peak viscosity, breakdown, and setback are all lowered by parboiling (Raghavendra Rao and Juliano 1970). The peak viscosity is the highest viscosity reached during the heating phase of the RVA process. At this point, a majority of granules are fully swollen but intact. For any particular type of starch, the more granules that are available to be hydrated, the higher the peak viscosity. During the high temperature hold phase at 95°C, the granules begin to break down, resulting in a drop in viscosity, and a trough (or hot paste) viscosity is recorded. As a result, native starch tends to have higher peak and trough viscosities than heat-treated starch. During parboiling, a variable amount of starch is pregelatinized, the extent of which is determined by the intensity of the parboiling. Hence, the higher the parboiling intensity, the fewer the amount of native granules available for hydration and, subsequently, the lower the peak and trough viscosities.

The numeric RVA results are shown in Table I and selected graphic results are shown in Fig. 1A and B. In addition to the normally reported RVA data, the % starch damage and a novel parameter, relative parboiling index (RPI), are shown in Table I. RPI was extremely useful in evaluating the overall effects of various treatment conditions. RPI was calculated using regression analysis with the % of starch damage as the dependent variable and the initial soaking temperature and steaming times as predictors. It is an indication of the severity of the parboiling process. The processing of cereals, like the milling of wheat and rice, causes a certain amount of mechanical disruption to the starch granules in the final product. The heat employed in parboiling rice gelatinizes some of the native starch present in the grain. The extent of this gelatinization depends on the intensity of the heat treatment during parboiling. Hence, the degree of parboiling can be estimated by measuring the extent of starch damage (mechanical disruption and gelatinization) in the parboiled rice. The level of starch damage directly affects the water absorption capacity and other properties, including quality characteristics, of the parboiled rice.

The peak viscosity of the raw milled sample from the RVA curve shown in Fig. 1A was 6,056 cP. This dropped drastically by

TABLE I
Percent Starch Damage (% SD), Relative Parboiling Index (RPI), and Rapid Visco Analysis (RVA) Measurements of Parboiled Rice Samples[a]

Sample	% SD	RPI	Viscosity (cP)					Peak Viscosity Time (min)	Pasting Temp (°C)
			Peak	Trough	Breakdown	Final	Setback		
Raw	1.08a	1.22a	6,056m	3,556n	2,500j	7,990m	4,434n	5.47a	76.70a
30–4	1.75b	1.61b	2,366k	2,167m	199g	4,190k	2,023m	5.73e	81.35c
30–8	1.82b–d	1.86bcd	2,087h	1,950k	137d	3,730i	1,780i	5.67d	81.30c
30–12	2.09e	2.11f	1,872e	1,759g	113b	3,319g	1,560g	5.80f	82.15d
50–4	1.84cd	1.71cd	2,169j	1,919j	250i	3,773j	1,854k	5.47a	80.65b
50–8	1.86d	1.96d	1,782c	1,603c	179e	3,042d	1,549g	5.60c	81.35c
50–12	2.31g	2.21g	1,866e	1,753g	113b	3,302g	1,439d	5.87g	81.45c
70–4	1.79bc	1.80bc	2,146i	1,900i	246i	3,712i	1,812j	5.53b	80.65b
70–8	2.23f	2.05e	1,939f	1,739f	200g	3,243f	1,504f	5.67d	81.35c
70–12	2.23f	2.30g	1,804d	1,613d	191f	2,962c	1,349c	5.67d	81.35c
90–4	1.85cd	1.89cd	2,003g	1,782h	221h	3,470h	1,688h	5.53b	80.55b
90–8	2.10e	2.15f	1,789c	1,656e	133cd	3,122e	1,466e	5.87g	81.45c
90–12	2.35g	2.40h	1,570b	1,439b	131c	2,576b	1,137b	5.80f	82.15d
Tilda	6.86h	9.42i	1,177a	1,143a	34a	1,837a	694a	6.60h	83.85e

[a] Values followed by the same letter in the same column are not significantly different at 5% level.

≈60% to 2,366 cP for sample 30-4. This was the mildest parboiled sample that had been soaked in water at 30°C and steamed for 4 min. Soaking at 30°C is not expected to result in pregelatinization of the starch granule. The source of this drastic change in the viscosity profile was therefore due solely to the steaming of the rice for 4 min. Subsequently, the peak viscosity dropped more gradually with the longer steaming times, as seen in Fig. 1A for samples soaked at 30°C. This also was the trend for increased soaking temperature for samples soaked at the same steaming time (Fig. 1B). The same trends were evident for trough, breakdown, final, and setback viscosities.

Table I also shows that both the time and pasting temperature at which the peak viscosity is reached increased in the same manner as the viscosity decreases. Thus, the pasting temperature of the raw milled sample (76.7°C) was significantly different from the pasting temperature of sample 30-4 (81.4°C) at the 5% level. Soaking in water at 30°C and steaming for 4 min resulted in an increase in pasting temperature of 4.7°C. This means mildly parboiling rice by steaming for 4 min results in pregelatinization of most of the starch granules that would have been gelatinized in paste between ≈77°C and ≈81°C. The pasting temperature and peak time for of the commercially parboiled sample were the highest, as expected.

The observed changes in pasting characteristics of rice from parboiling, particularly reduction of the extent of granule swelling, can be generally explained as the starch granules being disrupted by gelatinization and therefore not being in a position to swell as much as native starch. It could also be that the partial starch retrogradation following gelatinization (Ali and Bhattacharya 1976) binds the granular structure together and inhibits swelling.

Figure 2 shows DSC thermograms of selected samples (raw, 30-4, 90-12, and Tilda). Table II provides the data for all samples. The gelatinization temperature is actually a narrow temperature range at which starch granules begin to swell, lose crystallinity, and increase in viscosity. The exact temperature at which starch begins to undergo these changes is the gelatinization onset temperature. Generally, gelatinization enthalpy decreased as soaking temperature increased from 30 to 50°C and 70 to 90°C and the relative parboiling index (RPI) increased. At any particular soaking temperature, gelatinization enthalpy decreased as steaming times increased from 4 and 8 min to 12 min.

There were, however, some overlaps such as sample 30-12, which was soaked at 30°C and steamed for 12 min, having a lower enthalpy than sample 50-4, which was soaked at 50°C and steamed for 4 min. This means that sample 30-12 was more severely parboiled and had a higher RPI than sample 50-4. The same was the case for sample 50-12, which had a lower enthalpy than sample 70-4 and sample 70-12, which had lower enthalpy values than sample 90-4. The enthalpy of gelatinization for 90-12, the sever-

est parboiled sample in the laboratory, was 1.7 J/g. The enthalpy of gelatinization for the commercially parboiled sample was 0.3 J/g. Because most of the starch in the commercially parboiled sample was gelatinized, the gelatinization curve was virtually flat and the calorimeter could not detect the exact gelatinization temperatures.

Marshall et al (1993) has calculated the degree of gelatinization according to the formula $(1 - \Delta H_{par}/\Delta H_{raw})\ 100 = \%Gel$, where ΔH_{par} is enthalpy of gelatinization of the parboiled sample and ΔH_{raw} is enthalpy of the raw or native sample. This assumes that the raw sample contains no gelatinized starch. The results of this calculation are shown in Table II along with the gelatinization enthalpy. This indicates that ≈30% starch gelatinization is achieved only with the 30-4 treatment and that the 70-12 treatment gives twice that at 60%, which is almost as much gelatinization as with the 90-12 treatment. It also indicates that commercial parboiling still does not cause complete gelatinization. Along with X-ray diffraction results, this led some to believe (Jenkins and Donald 1998) that gelatinization occurs over a greater temperature range than DSC indicates.

Figure 3, along with the data in Table II, shows that the onset gelatinization temperature increases while gelatinization enthalpy decreases in a sawtooth manner. During partial gelatinization, it is thought that the diffused amylose molecules reorient and surround the amylopectin granules, which are already swollen by water penetration, and subsequently retrograde on cooling and storage. The increase in onset, peak, and conclusion temperatures is a general phenomenon that Biliaderis et al (1986) has proposed

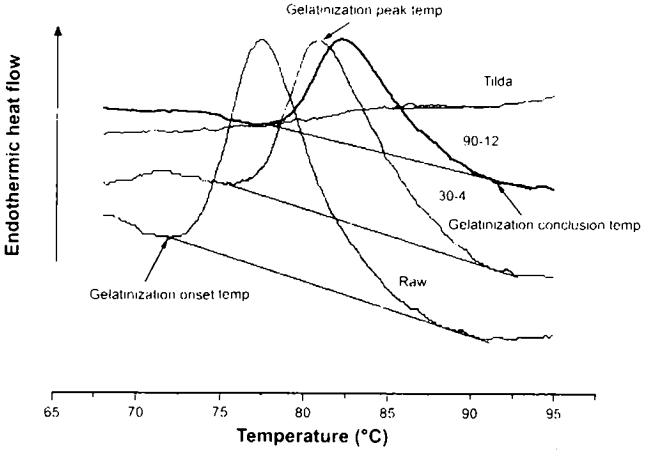

Fig. 2. DSC patterns of TX3108 raw, 30-4, 90-12, and commercially parboiled rice (Tilda).

TABLE II
Differential Scanning Calorimetry of Parboiled Rice Samples[a]

Sample	ΔH (J/gm)	% Gelatinization	T_o (°C)	T_p (°C)	T_c (°C)
Raw	5.31m	–	71.5a	77.0a	86.3a
30-4	3.73k	29.7k	76.1b	81.0bc	89.8e
30-8	3.69j	30.5j	76.9c	81.0bc	89.8e
30-12	2.78h	47.7h	77.3c	81.4cd	87.8b
50-4	2.98i	43.9i	76.1b	80.1b	88.8c
50-8	2.70g	49.2g	77.2dc	81.4cd	88.0b
50-12	2.43f	54.2f	78.4f	82.0d	89.8e
70-4	2.98i	43.9i	76.7c	80.4b	89.3d
70-8	2.42f	54.4f	77.0cd	80.4b	89.5d
70-12	2.10c	60.5c	79.0g	82.0d	88.9c
90-4	2.31e	56.5e	77.0cd	80.1b	88.0b
90-8	2.16d	59.2d	78.2f	82.0d	90.2f
90-12	1.72b	67.6b	79.0g	82.3d	90.4g
Tilda	0.34a	93.6a	–	–	–

[a] Values followed by the same letter in the same column are not significantly different at 5% level.

as being due to this partial melting, followed by recrystallization during cooling and subsequent sample storage.

Figure 4 and Table III show that focusing only on the carbonyl region of the Raman spectra and curve fitting to the amide I band gives an indication that conformational changes occur in protein upon parboiling. Five primary bands result from the curve-fitting process. These are at ≈1665 cm^{-1} for α-helix, ≈1665 cm^{-1} for random coil with hydrogen bonding, ≈1670 cm^{-1} for β-sheet, ≈1676 cm^{-1} for β-turn, and ≈1685 cm^{-1} for random coil with hydrogen bonding. In raw rice (Fig. 4A), most of the protein (66.0%) is in α-helix conformation as shown by the band at ≈1665 cm^{-1}. With only 4 min of steaming after soaking at 30°C, the amount of α-helix is reduced by ≈32%. This is consistent with RVA results that showed a dramatic drop in peak viscosity with this treatment. After this, there is only a gradual decrease in the α-helix component until the 50-12 sample, where it dips to <20%. For all the subsequent 12-hr steaming treatments, its contribution goes even lower. In the sample soaked at 90°C for 16 hr and steamed for 12 min (Fig. 4B), the amount of protein in the α-helix conformation is only 9.8%. The α-helix conformation has become the minor conformation. Much of it has been converted to random coil with hydrogen bonding (32.1%) and β-turn (24.2%). Tilda, the commercially parboiled sample (Fig. 4C), shows that more α-helix conformation is lost relative to the 90-12 sample, but the loss to 4.8% is not so dramatic. At what point the proteins (enzymes) are actually denatured cannot be determined by these measurements. However, their activity should be reduced significantly with a short steaming time.

Solid-state ^{13}C CP-MAS NMR spectra appeared to provide the most sensitive probe for the changes in starch structure. Figure 5

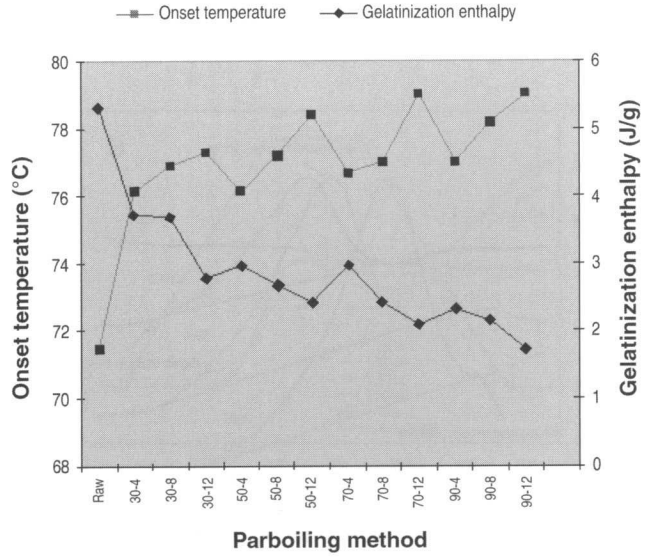

Fig. 3. Plot of onset temperature and gelatinization enthalpy vs. gelatinization temperature from DSC for all samples.

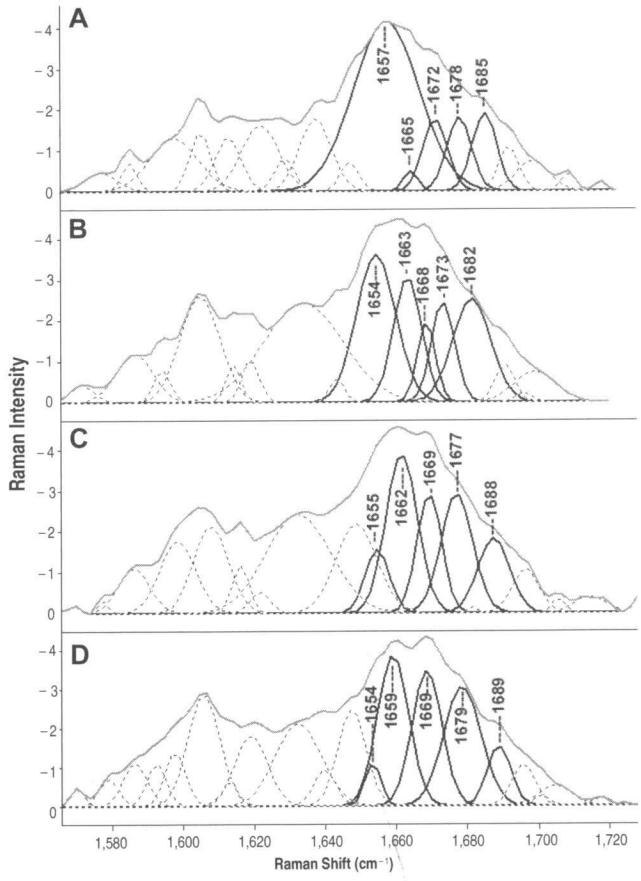

Fig. 4. Raman spectra with curve fitting to the carbonyl region, amide I, of protein: raw (**A**), 30-4 (**B**), 90-12 (**C**), and commercially parboiled rice (**D**). Relative contributions of the various conformations to the amide I band are solid black lines and others are dashed lines. Amide I conformations give bands for α-helix (≈1655 cm^{-1}), random coil with H-bonding (≈1665 cm^{-1}), β-sheet (≈1670 cm^{-1}), β-turn (≈1675 cm^{-1}), and random coil without H-bonding (≈1685 cm^{-1}).

TABLE III
Band Area (%) for Protein Conformations from Peak Fitting of Amide I Band of Raman Spectra of Parboiled Rice[a]

	α-helix	RC with HB	β-Sheet	β-Turn	RC w/o HB
Sample	**1,655 ± 5 cm^{-1}**	**1,665 ± 3 cm^{-1}**	**1,670 ± 3 cm^{-1}**	**1,676 ± 5 cm^{-1}**	**1,685 ± 5 cm^{-1}**
Raw	66.02	1.80	10.37	10.58	11.24
30-4	34.06	20.64	8.62	13.73	22.94
30-8	27.57	20.35	25.59	2.61	23.87
30-12	23.25	29.74	29.77	8.74	8.50
50-4	27.35	18.16	13.90	22.25	18.34
50-8	29.18	23.78	30.58	8.11	8.34
50-12	14.81	18.28	33.68	9.96	23.27
70-4	29.63	20.51	18.50	21.75	9.61
70-8	25.22	16.23	9.77	31.53	17.26
70-12	19.25	24.58	10.61	33.33	12.24
90-4	24.39	19.82	14.77	15.06	25.96
90-8	13.64	19.96	19.96	15.75	25.06
90-12	9.82	32.10	18.95	24.22	14.90
Tilda	4.79	32.32	27.66	30.49	9.53

[a] Raman shift with average deviation based on repetitive measurements and differences among samples.

shows the results obtained from the solid-state ^{13}C CP-MAS NMR spectra in the 108–90 ppm region covering the resonances due to the α-(1→4) and α-(1→6) anomeric carbons (C1) of starch, for the same four samples as shown in Fig. 4. Native cereal starches contain both amorphous components and crystalline components. The A-type polymorph of amylose, which exists as crystals in native rice starch, has been proposed to have a conformation of left-handed parallel-stranded double helices packed in the monoclinic space group C2 (B2 with c as unique axis) (Imberty et al 1988). In the representation of models for the B2 space group, where maltotriose is the repetitive unit, three equivalence classes are arrived at from symmetry operations. Thus, three different α-(1→4) linkages exist for of the A-type form. This ideally gives rise to three lines with intensities of 1:1:1 in the spectra for the anomeric (C1) resonances at 101, 100, and 99 ppm (Morgan et al 1995; Paris et al 1999). Thus, amylose of A-type (cereal) starches has become recognizable by the presence of a triplet for the anomeric carbons of the amylose component in the solid-state ^{13}C NMR spectra. These are shown clearly in the peak-fitting results of Fig. 5A-C. Here, the Fourier self-deconvolution, followed by peak-fitting, generated seven peaks for the partially parboiled samples. The gradual loss of the three narrow peaks and increase in broad components at 103 and 101-100 represents conversion to an amorphous and partially ordered structure. Glassy or amorphous (disordered) and partially-ordered interfacial (amylose or amylopectin) structures have been indicated to give rise to at least four broad C1 resonance lines at ≈103, 101-100, 98-97, and 94 ppm (Paris et al 2001). This change is very evident in Fig. 5D in the spectrum of the commercially parboiled starch. Peak areas for the C1 region were calculated from these results (Table IV). These results are consistent with deconvolution results obtained by Paris et al (1999, 2001) for the native and amorphous starch, respectively. The one exception is that an additional peak was generated in the 98 ppm spectral region for the partially parboiled samples. This has been attributed to α-(1→6) branching that is expected to have a wide distribution of chemical shifts because no hydrogen bond can exist to stabilize the branching points (Gidley et al 1993). This peak does not appear in the spectrum of the commercially parboiled rice but is supplanted by a broad peak at 101-100. It apparently replaces that of the remaining ordered structure of the 90-12 treated sample. The broad peak most likely represents some partially-ordered interfacial (amylose and amylopectin) structures. The peak at 94 ppm, according to Paris et al (1999), may be due to more constrained or entangled structures. This peak is not affected by the parboiling process.

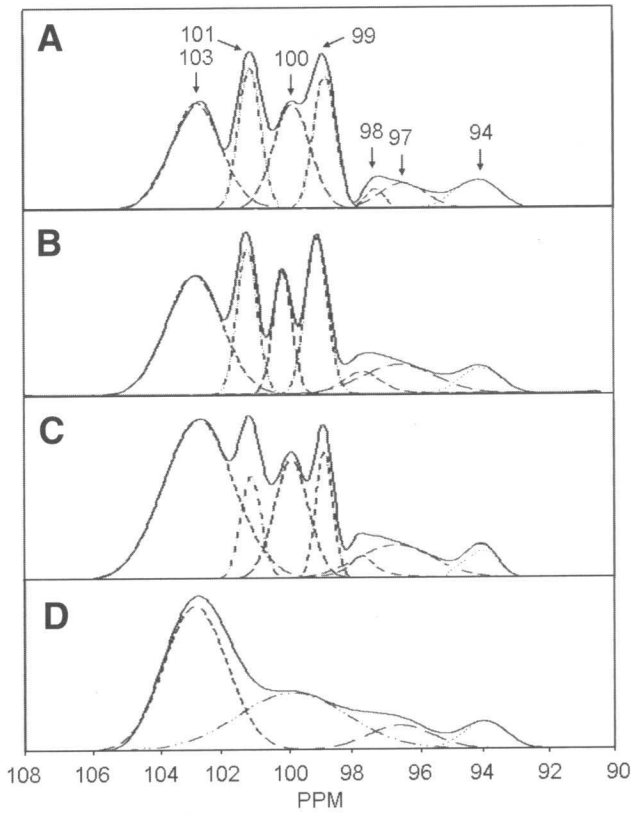

Fig. 5. Solid-state ^{13}C CP-MAS NMR spectra in the region of 108–90 ppm showing the curve fit peaks (dashed lines) to deconvoluted C1 trace (solid line) for starch of: raw (**A**), 30-4 (**B**), 90-12 (**C**), and commercially parboiled rice (**D**). Amorphous structures give broad peaks at 103, 101–100, 98–97, and 94 ppm. Amylose A-type crystalline conformers give narrow peaks at 101, 100, and 99 ppm.

CONCLUSIONS

RVA provides the overall assessment of the effects of soaking and steaming regimes for the parboiling of rice. The RPI is an indication of the severity of the parboiling process based on the combination of initial soaking temperature and steaming time. However, this assessment, along with DSC results, does not provide definitive information about what is specifically happening

TABLE IV
Peak Areas (%) After Deconvolution and Peak Fitting of Starch Anomeric Carbon (C1) Peak of ^{13}C CPMAS NMR Spectra of Parboiled Rice[a]

Sample	V_h/Amph 103[b]	A-Xta'l 101	A-Xta'l 100	A-Xta'l 99	Branch 98[b]	V_h/Amph 97[b]	Const 94
Raw	30.27	17.32	21.33	16.45	2.10	5.58	6.95
30-4	34.27	15.20	11.89	17.74	4.70	10.99	5.22
30-8	37.63	15.03	17.75	13.08	3.34	8.99	4.18
30-12	38.15	11.61	17.22	13.90	3.90	10.80	4.42
50-4	38.33	13.51	11.02	17.70	8.37	6.45	4.61
50-8	40.91	9.59	16.89	15.06	4.23	8.62	4.69
50-12	39.72	8.79	17.46	13.15	3.07	8.02	9.79
70-4	36.92	11.12	19.44	10.40	5.93	11.24	4.96
70-8	40.11	9.98	18.67	10.28	3.75	13.42	3.81
70-12	39.81	10.65	14.54	13.55	5.11	10.38	5.95
90-4	43.76	9.88	10.09	19.38	5.54	6.27	5.08
90-8	46.84	8.39	12.34	15.64	4.62	7.80	4.37
90-12	51.22	9.79	19.00	0.19	3.71	11.58	4.51
Tilda	50.21	0.00	34.67[b]	0.00	0.00	8.63	6.49

[a] Chemical shift in ppm from DSS (sodium 2, 2-dimethyl-2-silapentane-5-sulfonate).
[b] Broad peak, V_h, or noncrystalline material (partially ordered interfacial or amorphous amylose or amylopectin).

to the rice chemical components of protein and starch due to various treatments. Raman and solid-state ^{13}C CP-MAS NMR spectra are excellent probes for changes in the conformation of the protein and starch components of rice, respectively. Using Raman spectroscopy to further assess the effectiveness of partial parboiling treatments such as those found in the artisanal rice industry of Ghana has shown that they easily facilitate denaturization of the protein. Thus enzymes could be inactivated and fermentation of the rice could be retarded with a steaming time of only 4 min. The use of solid-state NMR has shown that significant gelatinization of the starch is accomplished with soaking at 90°C and steaming rice for 12 min. In addition, it indicates that the percent of V_h/amorphous plus the remaining crystalline starch in the 90-12 treatment is equal to the percent amorphous and partially-ordered (amylose and amylopectin) starch in commercially parboiled rice. Thus, even in commercially parboiled rice, all the starch components do not assume one amorphous structure. This result is consistent with calculations of percent gelatinization from DSC results that indicate that ≈68% of the starch is gelatinized with the 90-12 treatment. Partial parboiling, 90°C soaking, and >8 min steaming (ideally ≈12 min) should be sufficient to prevent the rice from spoiling and enable annealing of the rice. This will ensure that high levels of breakage do not occur from milling and allow the rice to be stored for long periods of time.

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